

STUDIES OF POLARISED ETHYLENES

BY

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1972

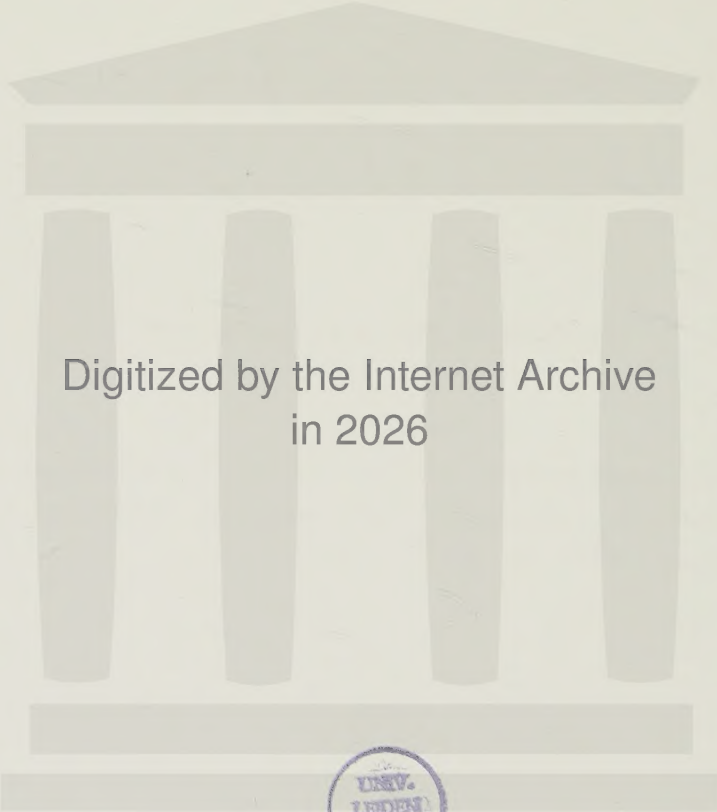
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Ingegerd Wennerbeck, fil.mag., B1

AVHANDLING FÖR DOKTORSEXAMEN

Avhandlingen kommer att försvaras vid en offentlig disputation i hörsal A, Kemicentrum, lördagen den 7 oktober 1972 kl. 10¹⁵.

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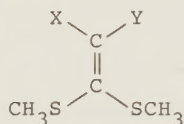


This review summarizes results from the following papers which will be referred to by the Roman numerals I-V.

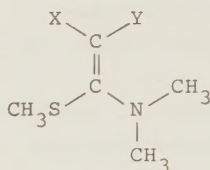
- I. Sandström, J. and Wennerbeck, I., Studies of Polarised Ethylenes. Part I. Barriers to Rotation Around the Carbon-Carbon Double Bond in 1,1-Bis-alkylthio-ethylenes. Acta Chem. Scand. 24 (1970) 1191.
- II. Eriksson, E., Sandström, J. and Wennerbeck, I., Studies of Polarised Ethylenes. Part II. Preparation of 1,1-Bis-dimethylamino-ethylenes and 1,3-Dimethyl-2-methylene-imidazolidines. Acta Chem. Scand. 24 (1970) 3102.
- III. Sandström, J. and Wennerbeck, I., Conformational Study of Twisted Ethylenes by Nuclear Magnetic Resonance Spectroscopy. Chem. Commun. 1971, 1088.
- IV. Wennerbeck, I. and Sandström, J., Studies of Polarised Ethylenes. Part IV. Barriers to Rotation Around Formal Double Bonds and Formal Single Bonds in 1,1-Bis-dimethyl-amino-ethylenes. Organic Magnetic Resonance, in press.
- V. Wennerbeck, I., Studies of Polarised Ethylenes. Part V. Ultraviolet Spectra: Experimental Results and P.P.P. Calculations. Acta Chem. Scand., in press.

ABSTRACT

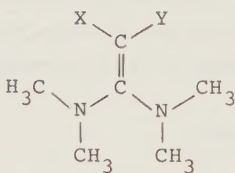
Barriers to internal rotation and other physical properties have been investigated in four types of ethylenes substituted by pairs of groups exerting a push-pull effect. The compounds studied are: 1,1-bis-alkylthioethylenes (A), 1-alkylthio-1-dimethylaminoethylenes (B), 1,1-bis-dimethylaminoethylenes (C) and 1,3-dimethyl-2-methyleneimidazolidines (D). The different combinations of electron-attracting substituents X and Y are denoted by numbers 1-11.



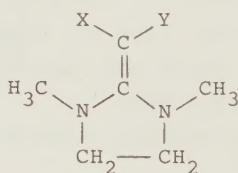
A



B



C



D

	X	Y
1.	CH ₃ OCO	CN
2.	PhCO	CN
3.	CN	CN
4.	p-NO ₂ C ₆ H ₄	CN
5.	Ph	CN

	X	Y
6.	Ph	COCH ₃
7.	PhCO	COCH ₃
8.	CH ₃ CO	COCH ₃
9.	CH ₃ OCO	COCH ₃
10.	CH ₃ OCO	CO ₂ CH ₃
11.	PhCO	CO ₂ C ₂ H ₅

In the series of 1,1-bis-alkylthioethylenes and oxidized derivatives the following compounds (E) have also been prepared and studied:

	X	Y	A	B
$ \begin{array}{c} \text{X} \quad \text{Y} \\ \diagdown \quad \diagup \\ \text{C} \\ \\ \text{C} \\ \diagup \quad \diagdown \\ \text{A} \quad \text{B} \\ \text{E} \end{array} $	1. CH_3OCO	CN	CH_3S	SCH_2Ph
	2. CH_3OCO	CN	PhCH_2S	SCH_2Ph
	3. H_2NCO	CN	CH_3S	SCH_3
	4. PhCO	$\text{CO}_2\text{C}_2\text{H}_5$	CH_3SO_2	SO_2CH_3
	5. CH_3CO	H	CH_3S	SCH_3

The free energies of activation ($\Delta G^\ddagger$) for rotation around the C=C bond have been determined by the NMR lineshape method for compounds 1A-10A and 1C-10C except for 3A, 8A, 10A and 3C, 8C, 10C, where the substituents X and Y are the same.

In the series of compounds D the $\Delta G^\ddagger$ value for the rotation around the C=C bond has only been determined for compound 5D. The temperature-dependent NMR spectra of compounds 2D, 6D, 7D, 8D and 11D show that the molecules are twisted around the carbon-carbon double bond.

Hindered internal rotation around the C-N bonds has been observed in compounds 1C-10C, and in some of these compounds $\Delta G^\ddagger$ values for restricted rotation around the C-X and/or C-Y bonds have also been estimated.

In order to obtain the activation parameters for the hindered rotation around the C=C bond in 2A and 5C complete lineshape analyses were performed. Furthermore, the activation parameters for the rotation around the C-N bonds in 5C were determined by the same method.

The assignment of signals to methyl groups in compounds 1C-10C has been undertaken with the aid of aromatic solvent induced shifts (ASIS).

MO calculations by the HMO method, as well as by an HMO method with α, β -variation have been made for compounds 1A-10A and a reasonable linear correlation was obtained between the differences in π -electron energy (calculated by the HMO method) between initial and transition states and $\Delta G^\ddagger$ values for the hindered rotation around the C=C bond.

Infrared spectra have been recorded for 1A-10A and 1C-10C and it is quite evident from these data that the compounds are strongly conjugated.

A UV study of all the compounds 1A,B,C,D-10A,B,C,D has been undertaken, and for the compounds, 1A-1D, 3A-3D, 8A-8D, 10A-10D, the experimental data have been correlated with transition energies and oscillator strengths calculated by the SCF-CI method in the Pariser-Parr-Pople version.

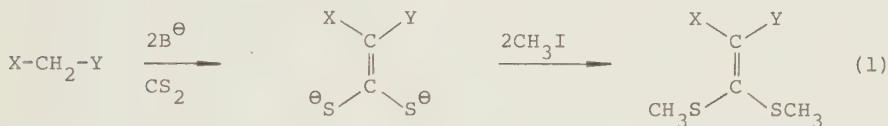
INTRODUCTION

The well known steric stability of simple ethylenes is due to interaction between two p-orbitals on the two sp^2 -hybridized carbon atoms. The interaction causes high energy barriers separating cis and trans forms of such ethylenes as 1,2-dideuterioethylene¹ (61.2 kcal/mol) and 2-butene² (58 kcal/mol). However, these barriers are considerably lowered in ethylenes with electron-accepting and electron-donating substituents. The first NMR spectroscopic investigation of a C=C bond rotation was made by Kende³ et al. in formyl derivatives of pentatrifulvalenes. These rotations are assumed to involve dipolar transition states, where the cyclopentadienyl system stabilizes the negative charge and the cyclopropenyl system stabilizes the cationic centre.

This polar mechanism for the rotation around the C=C bond has been found to be valid for many other systems, such as enamines^{4,5,6,7,11}, ketene-mercaptoaminals⁸ and keteneaminals.^{9,10} In many of these systems^{5,6,9,10,11} restricted rotations around the C-N bonds have also been observed and in some cases even around the C-X and/or C-Y bonds.¹⁰ The energy barriers for the C-N rotational process are due to loss of conjugation energy on going from the planar initial state to the nonplanar transition state. The intention of the study of the above series of polarised ethylenes was to find correlations between the structural parameters and the measured properties of the compounds.

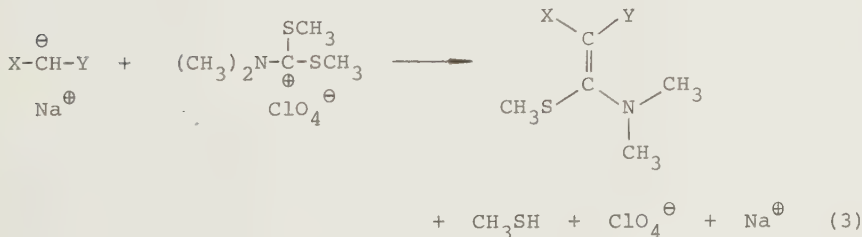
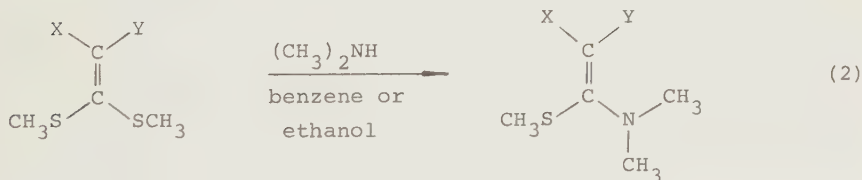
SYNTHESIS

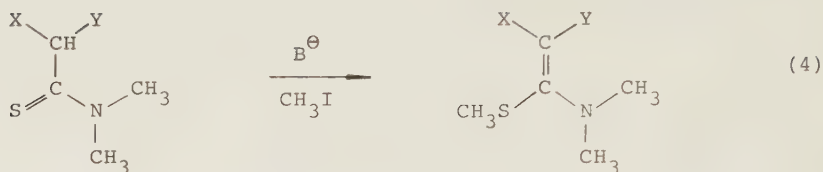
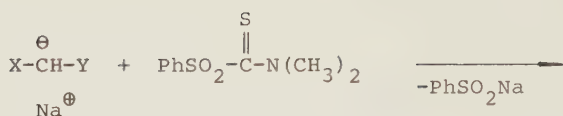
Compounds A and E have mainly been prepared using the method developed by Gompper and Töpfl.¹²



Sodium hydride was used as base, and benzene containing dimethylformamide (DMF) or hexamethyl phosphoric triamide (HMP) was used as solvent. For a detailed description see I.

The synthesis of the compounds B was carried out according to one of the following three methods (eqs 2-4):

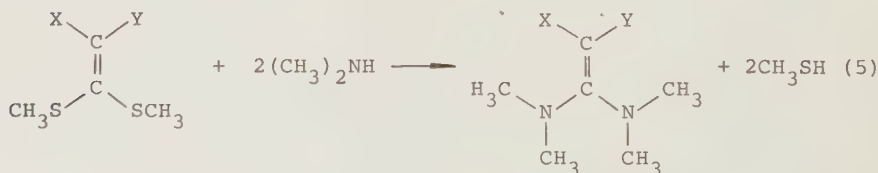


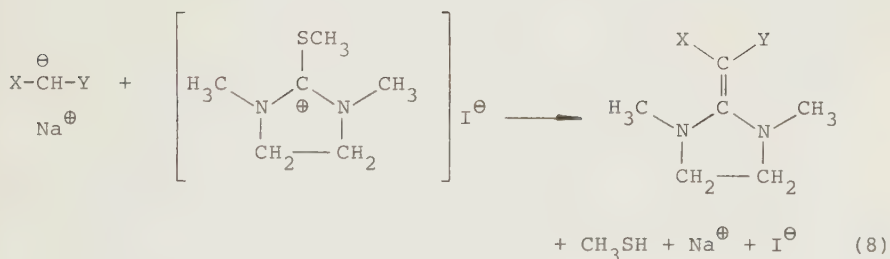
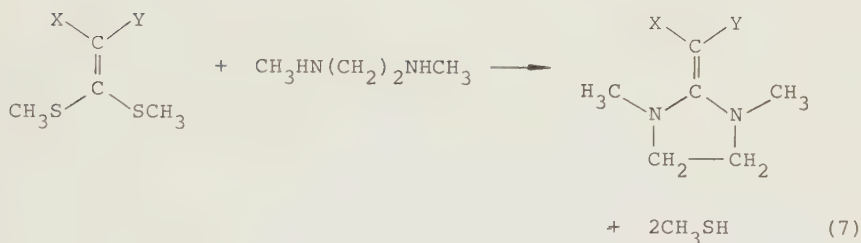
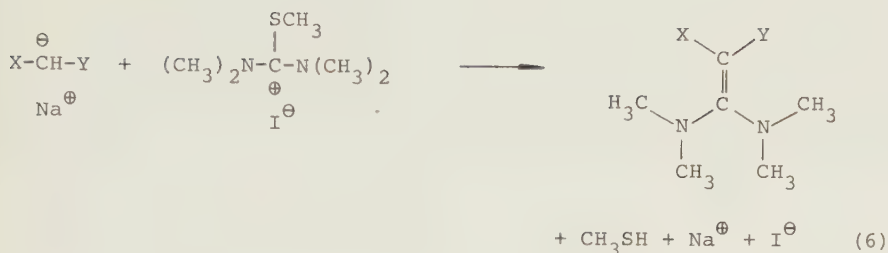


Compounds 1B, 2B, 3B, 7B, 8B, 9B and 10B have been prepared according to the method shown in eq (2), which illustrates the method used by Gompper¹³ et al. for the preparation of 1B. Preparation of 8B and 9B are described in Ref. 14. Compounds 3B and 9B are described by Nakai¹⁵ using the method given in eq (3). This method was also applied to the preparation of 4B. Shvo⁸ et al. report yet another method for the preparation of 10B.

The N,N-dimethylthioamide of eq (4) was made according to a method given in Ref. 16 and compounds 5B and 6B were obtained in conformity with this equation. Sodium hydroxide was used as base in the preparation of 5B and sodium hydride in the preparation of 6B. Furthermore, compound 6B was isolated as a crystalline picrate. A detailed account of the experimental methods and data will be given in a forthcoming paper.¹⁷

Paper II deals with the synthesis of compounds of the types C and D. These compounds were prepared in conformity with eqs (5), (6) and (7), (8), respectively.





The methods represented in eqs (5) and (7) have been used by Gompper¹³ *et al.* when they prepared compounds similar to C and D.

Kessler¹⁰ has prepared a series of 1,1-bis-dimethylamino-2-aryl-2-cyanoethylenes by a method similar to that shown in eq (6). The reactions between the corresponding 1,1-bis-methylthioethylenes (A) and dimethylamine have been performed under different conditions. Thus, compounds 8C and 9C reacted at room temperature, 2C on refluxing in benzene, while 1C, 6C and 7C required heating with dimethylamine in benzene in sealed tubes at 120-150°C. Compounds 3C, 4C, 5C and 10C were prepared according to eq (6). Compound 3C

is also described in Ref. 18, and 4C and 5C in Ref. 10.

Among the compounds D only 4D required heating in a sealed tube at 120°C with N,N'-dimethylethylenediamine in benzene. 1D, 2D, 7D, 8D and 9D reacted by refluxing with this reagent in benzene. The method given in eq (8) was used when 3D, 5D, 6D and 10D were prepared.

NMR measurements

To determine barriers to internal rotation in the range of 7-25 kcal/mol the dynamic nuclear magnetic resonance spectroscopy method (DNMR) is suitable. This method originates from the theory for exchange broadening of NMR signals developed by Gutowsky¹⁹ et al. Binsch²⁰ has published an extensive review of the use of DNMR in the study of intramolecular rate processes.

The free energies of activation, $\Delta G^\ddagger$, have been used as a measure of the barrier height. In most cases $\Delta G^\ddagger$ has been determined at the coalescence temperature utilising the approximate expression²¹

$$k = \frac{\pi \cdot \Delta \nu_0}{\sqrt{2}} \quad (9)$$

and the Eyring equation²². The $\Delta G^\ddagger$ values obtained for compounds A are listed in I, Table 1.

The free energies of activation for both the rotation around the C=C bond and that around the C-N bonds in compounds C are tabulated in IV, Table 3. The values of $\Delta G^\ddagger$ for the hindered rotation around the C=C bond and C-N bond in the 1-methylthio-1-dimethylaminoethylenes (B) will be published in a forthcoming paper¹⁷.

In order to obtain $\Delta S^\ddagger$ and $\Delta H^\ddagger$ values for the C=C and C-N rotations in 5C, a complete lineshape study over a larger temperature interval was undertaken (IV, Table 5). The same method was used to estimate $\Delta S^\ddagger$ and $\Delta H^\ddagger$ for the C=C rotation to compound

2A (I, Table 2). Furthermore, the rate of the isomerisation of one of the isomers of 1E was studied by integration at four temperatures (I, Table 3).

In compounds 1C, 2C, and 4C the temperature-dependent NMR spectra are simultaneously affected by the C=C rotation and both C-N rotations, and in 2C also by the acyl rotation. The rate constants for the restricted rotations in these compounds were obtained with the aid of a computer program allowing for exchange among up to eight sites (see IV).

The ASIS effect

It has been proposed by many authors (see the review by Laszlo²³), that formation of loose collision complexes occurs between aromatic solvent molecules and polar solutes, such as N,N-dimethylamides and -thioamides, which affects the shifts of the N-methyl signals in these compounds in a specific way. This effect is often referred to as the ASIS effect (Aromatic Solvent Induced Shift).

This phenomenon is observed in the compounds C and D (see IV, Fig. 2) and when it was desirable to assign the individual signals to methyl groups or at least to pairs of methyl groups the ASIS effect was utilised. Furthermore, this effect has been used to distinguish between restricted rotation around the C=C and the C-N bonds in the compounds C (IV, Table 2), when the interpretation of the temperature-dependent NMR spectra was doubtful (IV).

Discussion of the activation parameters

If the idea of a completely polarised transition state is accepted, the barrier to rotation around the C=C bond in a polarised ethylene is determined by the following factors:

- 1) The capacity of the electron-donating part of the molecule (A-C-B)[⊕] to stabilize a positive charge (barrier lowering);

- 2) the capacity of $(X-C-Y)^{\ominus}$ to stabilize a negative charge (barrier-lowering);
- 3) the electronic interaction in the initial state (barrier-raising), and
- 4) steric interactions between A and X, B and Y, A and B and X and Y.

The importance of effect 1 is demonstrated by the differences between 1,1-bis-alkylthioethylenes and 1,1-bis-dimethylaminoethylenes with the same sets of X and Y. The barriers to rotation around the C=C bond are substantially lower in the latter type of compounds. The gross importance of effect 2 is also well demonstrated in both series A and C. However, the superposition of effects 1-3 sometimes leads to a change in order of the barriers as a function of X and Y in the different series with respect to A and B.

The steric effect between A and B is evident in the 1,1-bis-dimethylaminoethylenes. The repulsion between the dimethylamino groups forces them to rotate out of the plane of the double bond, thereby diminishing their contribution to effects 1 and 3 and also decreasing their steric interactions with X and Y.

In compounds D, the electron-donating effect of the nitrogen atoms can operate more efficiently than in compounds C, which decreases the energy difference between the planar and the 90° twisted states. Furthermore, the steric interactions between the N-methyl groups and X and Y are increased. In 5D, the planar state is still more stable than the 90° twisted state. With increasing size and electronic effects of X and Y the energetic relationships are reversed and the twisted state becomes the more stable one (III). This is conclusively demonstrated by exchanging the N-methyl groups for prochiral benzyl groups. In the twisted molecule the benzylic protons are non-equivalent (Fig. 1), and in the slow rotation limit they give AB spectra. In a compound of this type with $X = CH_3CO$, $Y = CPh$, the barrier to rotation around the double bond is 16.4 kcal/mol, but in this case the transition state is at least approximately represented by the planar structure (III).

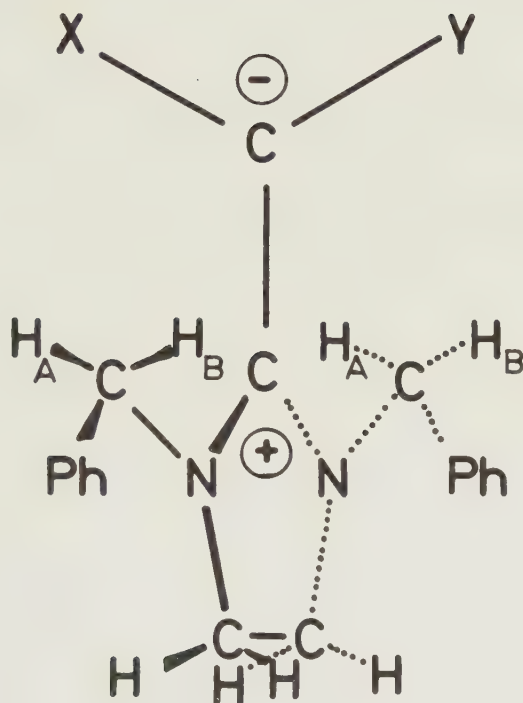


Fig. 1. Twisted structure of a molecule of type D with N-benzyl groups

In compound 8D the barrier to hindered rotation around the $\text{C}-\text{C}-\text{CH}_3$ bond has been determined to be 13.5 kcal/mol, while the same barrier in 8C has a $\Delta G^\ddagger$ value of 10.2 kcal/mol (IV, Table 6b). These experimental data indicate that compounds D have a more negative carbanion part $(\text{X}-\text{C}-\text{Y})^-$ than compounds C.

Rotation around the C-N bonds in the 1,1-bis-dimethylamino-ethylenes involves transition states which are less polar than the initial state, since there is a loss in conjugation on twisting a dimethylamino group 90° out of the plane. The barriers to rotation around the C-N bonds are affected by three factors:

1) Stabilization of the initial state through conjugation (barrier-raising);

2) stabilization of the transition state through π -electron delocalization (barrier-lowering);

3) the ability of the dimethylamino groups to be in the molecular plane in the initial state (barrier-lowering, if the dimethylamino groups are forced out of the plane by X and/or Y).

The difference between effects 1 and 2 can be expected to be larger, the more efficient the interactions between the electron-donating and electron-attracting parts of the molecule, which causes compounds with low C=C barriers to have high C-N barriers and vice versa. Kessler¹⁰ also observed this behaviour in a series of 1,1-bis-dimethylamino-2-cyano-2-(p-substituted phenyl)ethylenes.

The effects of combinations of X and Y depend also on the electron-donating parts of the molecules. It is therefore rather hazardous to transfer substituent effects from one group of polarized ethylenes to another (IV, Table 7).

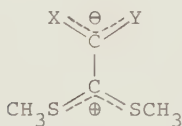
In general the C-N barriers seem to be less influenced by solvent polarity than the C=C barriers as a consequence of the less polar transition state attained during the C-N rotation. Nevertheless a large negative entropy of activation has been found for the C-N rotations in 5C. The less the polarity of the molecule is diminished on going from the initial to the transition state, the more negative the $\Delta S^\ddagger$ value will be. The explanation of the negative $\Delta S^\ddagger$ for the C-N rotations in 5C may be that the two dimethylamino groups are not in the molecular plane, but are twisted about 20° around the C-N bonds²⁴. When one of them is rotated the other can rotate into the molecular plane, which will at least partly compensate for the loss of polarity.

The negative $\Delta S^\ddagger$ values for the C=C rotation in 2A, 5A and 1E are in good agreement with the assumed changes in polarity on rotation. The less negative $\Delta S^\ddagger$ value for 5C, compared to that for 2A and 1E, indicates a larger ground state polarization or at least a smaller change in the solvation shell on rotation in 5C.

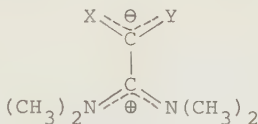
IR studies

The infrared spectra of compounds A and C have been recorded and the characteristic absorption bands are tabulated in I, Table 6 and in IV, Table 8, respectively.

From the IR spectra, it is evident that these compounds are polarised. Considering the nature of the X and Y substituents the polarisation is assumed to have the directions indicated by F and G.



F



G

Conjugation of the dimethylamino and alkylthio groups with the double bond causes in all compounds a more pronounced lowering of the frequency of the substituents -C≡N and $\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-}$ than simple α,β -unsaturation. These results are in agreement with those found by Gompfer^{12,13,25} et al. and Jensen²⁶ et al. in analogous compounds.

Inspection of the nitrile frequencies shows that compounds 1C-5C ($\nu_{\text{C}\equiv\text{N}} = 2150\text{-}2190\text{ cm}^{-1}$) are more polarised than the analogs 1A-5A ($\nu_{\text{C}\equiv\text{N}} = 2199\text{-}2209\text{ cm}^{-1}$). This result is in agreement with the fact that the $\Delta G^\ddagger$ values for restricted rotation around the C=C bond in 1,1-bis-dimethylaminoethylenes (IV, Table 3) are lower than in 1,1-bis-alkylthioethylenes (I, Table 1).

The formal positive charge on the nitrogens in the resonance structure G causes an increase in the CH₃-N stretching frequencies ($\nu_{\text{CH}_3\text{-N}} = 1400\text{-}1440\text{ cm}^{-1}$) compared to those of ordinary tertiary aliphatic amines ($\nu_{\text{CH}_3\text{-N}} = 1000\text{-}1300\text{ cm}^{-1}$).²⁷

The IR spectrum of compound 4E (I, Table 6) shows normal unconjugated ester and benzoyl carbonyl frequencies, which indicates that it is important with electron-donating substituents to get

polarisation of the central bond.

UV studies

A UV study of compounds 1A,B,C,D-10A,B,C,D has been undertaken in order to investigate the electronic transitions in these compounds (V). Molecular orbital calculations using the semi-empirical Pariser-Parr-Pople LCAO-SCF-CI method²⁸ in two versions were carried out on compounds 1A-1D, 3A-3D, 8A-8D, and 10A-10D. The difference between the two methods used lies in the evaluation of the integrals of the Fock matrix (V). Method 2 is one proposed by Roos²⁹ et al.

It was found that the agreement between calculated and experimental absorption maxima was not very satisfactory. The deviations were larger with method 2 than with method 1. This may be explained by the fact that method 2 has not been parametrized for those systems.

Compounds B in most series have $\pi \rightarrow \pi^*$ absorption bands at the longest wavelength and this is contrary to the result of UV studies of analogous thiocarbonyl compounds³⁰, where the trithiocarbonate (corresponding to compounds A) absorbs at the longest wavelength.

To verify the suggestion that compounds D are twisted around the double bond (III), the UV spectra of the tetrabutylammonium salts of sodium salts of the active methylene compounds $X-CH_2-Y$ were recorded. As expected, in most series the absorption bands of compounds D were shifted in the direction of the absorption maxima of the anions compared to those of the corresponding compounds C.

The UV spectra of compounds 1A-1D, 3A-3D, 8A-8D were recorded in both cyclohexane and ethanol, and the increase in the polarity of the solvent resulted in hypsochromic (compounds C and D) or bathochromic shifts (compounds A). Compounds B, except 10B, were not affected by changing the solvent. These solvent effects can be ascribed to changes in charge distribution on excitation. MO calculations of the charge distributions in the initial and excited states (V, Figs. 1 and 2) reproduced the observed trend.

MO calculations

Electron distributions and orbital energies for compounds 1A-10A have been calculated by the HMO method and by an HMO method with α, β -variation³¹. The results are tabulated in I, Table 5.

The π -electron energy contribution to the barrier, ΔE_{π} , is given by the expression

$$\Delta E_{\pi} = E_{\pi, \text{XYC}} - (E_{\pi, \text{XYC}})^{\ominus} + E_{\pi, \text{(RS)}} - (E_{\pi, \text{(RS)}})^{\oplus}$$

The ΔE_{π} values obtained by the HMO method according to the above formula give a reasonable linear correlation with $\Delta G^{\ddagger}$ (I, Fig. 1). Furthermore, there exists a fairly good correlation between $\Delta G^{\ddagger}$ and the π -bond order of the C=C bond (I, Fig. 1).

The calculations of the π -bond orders for the C=C bond in 1A with both the HMO (α, β -variation) method and the P.P.P. methods gave the same result, i.e. the double bond character is essentially preserved in 1,1-bis-alkylthioethylenes.

The calculated π -electron charges on the central carbon atoms in 3A and 3C (V, Table 6) indicate that 3C would have the largest dipole moment. This has been verified by determination of the dipole moments³², which are 6.16 D and 7.84 D, respectively.

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